INTRODUCTION

Amphiboles are a complex group of hydroxyl-bearing minerals in which solid solution may occur at all cation sites, and also at the anion site O3, which may be occupied by OH−, F−, Cl−, and O2−. For O3 = O2−, local bond-valence requirements are satisfied by the occurrence of highly charged octahedral cations occurring either at the adjacent M1 site (Ti) or at the M1 and M3 sites (Fe3+ and Mn3+). Amphiboles may crystallize with variable amounts of monovalent (OH−, F−, Cl−) and divalent (O2−) anions at O3, but loss of hydrogen may also occur post-crystallization due, for instance, to an increase in T or decrease in P (e.g., during subduction processes or volcanic eruptions). In the latter case, extensive experimental studies on dehydrogenation obtained by thermal treatment in both natural and synthetic amphiboles (e.g., Barnes 1930; Addison et al. 1962a, 1962b; Ernst and Wai 1970; Ungaretti 1980; Phillips et al. 1989; Popp et al. 1995a, 1995b) have shown that the amount of O2− is correlated with the amount of Fe3+ produced by the accompanying oxidation. Much of this work was done using Mössbauer or infrared spectroscopy as probes to monitor the change in iron oxidation state, loss of H, and atomic adjustments within the structure, such as displacement of Na from the M4 site to the A site in sodic amphiboles (e.g., Ernst and Wai 1970).

Systematic analysis of natural amphiboles shows that crystals with major amounts of O2− at O3 contain major amounts of Ti4+ and Fe3+. The association between Ti4+ and OH-deficiency has long been recognized in calcic amphiboles (kaersutites, with Ti > 0.50 atoms per formula unit, apfu; Leake 1968; Saxena and Ekstrom 1970), and neutron-diffraction refinement (Kitamura and Tokonami 1971; Kitamura et al. 1973, 1975; Jirak et al. 1986; Pechar et al. 1989) has shown that Ti is partly or completely ordered at the M1 site. More recently, Oberti et al. (1992) showed significant amounts of O2− in sodic-calcic amphiboles, thus showing that coupling with an O2− anion through an A-cation significantly affects band position. Infrared spectroscopy can detect the presence of O2− in amphiboles in chemically favorable cases, i.e., in the absence of F. Moreover, the FTIR spectra show that all octahedral configurations involving M1Ti4+ or M1Fe3+ + M3Fe3+ are associated with O2− at both adjacent O3 sites, and that M1Al is locally associated with OH, confirming SRO models based on structure refinement results.

Keywords: Ti-rich pargasite, Lherz (French Pyrenees), single-crystal FTIR spectroscopy, anion occupancy.

ABSTRACT

This paper reports a single-crystal unpolarized-light FTIR study in the OH-stretching region of a suite of well-characterized Ti-rich pargasites from Lherz (French Pyrenees). All amphiboles studied have fairly constant M-site composition, with [6]Altot ~0.55 atoms per formula unit (apfu), [6]Ti ~0.45 apfu, and [6]Fe3+ ~0.40 apfu. SIMS and SREF data show all samples to have an O3 anion composition of OH = O2− = 1.0 apfu, with negligible F. The FTIR spectra show for all samples a broad absorption consisting of several overlapping bands; three main components can be recognized: ~3710, 3686, and 3660 cm−1, respectively, with an asymmetric tail extending to lower frequency. Six Gaussian components can be fitted to the spectra; comparison with spectra of both synthetic and natural pargasites allows five of these components to be assigned to local configurations involving OH-O2− at the O3 site, thus showing that coupling with an O2− anion through an A-cation significantly affects band position. Infrared spectroscopy can detect the presence of O2− in amphiboles in chemically favorable cases, i.e., in the absence of F. Moreover, the FTIR spectra show that all octahedral configurations involving M1Ti4+ or M1Fe3+ + M3Fe3+ are associated with O2− at both adjacent O3 sites, and that M1Al is locally associated with OH, confirming SRO models based on structure refinement results.

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FTIR spectroscopy of Ti-rich pargasites from Lherz and the detection of O2− at the anionic O3 site in amphiboles

GIANCARLO DELLA VENTURA,1,2,* ROBERTA OBERTI,2 FRANK C. HAWTHORNE,3 AND FABIO BELLATRECCIA1

1Dipartimento di Scienze Geologiche, Università Roma Tre, Largo S. Leonardo Murialdo 1, I-00146 Roma, Italy
2CNR-Istituto di Geoscienze e Georisorse, Unità di Pavia, via Ferrata 1, I-27100 Pavia, Italy
3Department of Geological Sciences, University of Manitoba, Winnipeg, R3T 2N2 Canada

E-mail: dellaven@uniroma3.it

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1Dipartimento di Scienze Geologiche, Università Roma Tre, Largo S. Leonardo Murialdo 1, I-00146 Roma, Italy
2CNR-Istituto di Geoscienze e Georisorse, Unità di Pavia, via Ferrata 1, I-27100 Pavia, Italy
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